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Modified Adam–Gibbs models based on free volume concept and their application in the enthalpy relaxation of glassy polystyrene

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ABSTRACT

Vogel–Fulcher–Tammann (VFT) equation based on free volume concept is used extensively to describe the temperature dependence of relaxation time of polymer above the glass transition temperature T_g, but failed in fitting the enthalpy relaxation data across the glass transition region. Under the line of the Adam–Gibbs theory on temperature dependence of cooperative relaxation property, two equations based on the free-volume theory of glass transition, free-volume (FV) and modified free-volume (FVM) equations, were proposed and applied to fit the enthalpy relaxation data of PS. Compared with the VFT equation, the fitting quality of FV equation is improved greatly and similar to that of the extensively used Tools–Narayanaswamy–Moynihan (TNM) and Adam–Gibbs (AG) models. The fitting quality of FVM equation is improved further and better than that of TNM and AG models, as well as Macedo model with the same number of fitting parameters, especially on the prediction of the limit fictive temperatures.

1. Introduction

Relaxation is an outstanding character of polymer material in the aspects of structure, volume, enthalpy, mechanical property and dielectric property etc. Marked departure from the Arrhenius equation with a temperature independent activation energy was shown in the temperature dependence of the relaxation, especially when the temperature is around the glass transition temperature T_g. An extensively used model to describe the temperature dependence of relaxation time of polymer is the Williams–Landel–Ferry (WLF) equation [1] which originated from Vogel–Fulcher–Tammann (VFT) law (or named Vogel law) based on the free volume concept [2–4]:

$$\tau = A\exp\left(\frac{D}{T-T_0}\right) \tag{1}$$

where A, D and T_0 are model constants, T is temperature, respectively. By introducing a parameter T_0 at which the relaxation time has infinite value, VFT equation has the advantage of having a temperature dependent activation energy.

The models of relaxation time are linked with the viscosity theory tightly. Based on a solid theoretical, assuming a distribution of hole sizes exists, and the jump probability is determined only by the chance of finding an adjacent local free volume of sufficient size to jump into, Cohen and Turnbull derived the expression below [5]:

$$\eta(\tau) = A\exp\left(\frac{B}{f}\right) \tag{2}$$

where f is the fractional free volume and A and B are constants, the latter being about unity. Putting $f \sim T - T_0$, Eq. (1) is obtained. Macedo and Litovitz have criticized the usual free-volume derivations for neglecting the thermal activation needed for a particle to move from one pocket of free volume to another and derived the hybrid expression [6]:

$$\eta(\tau) = A\exp\left(\frac{B}{f}+\frac{E}{RT}\right) = A\exp\left(\frac{D}{T-T_0}+\frac{E}{RT}\right). \tag{3}$$

Recently, Mauro–Yue–Ellison–Gupta–Allan model [7] and Chandler model [8,9] with more parameters were reported to show better agreement with the experimental data than does the VFT equation.

Whereas it was recognized that relaxation time τ, the key parameter in the description of the relaxation dynamics, is both temperature and structure dependent. The nonlinearity character of relaxation has been revealed by Kovacs decades ago by measuring minutely the volume relaxation following a series of single- and two-step temperature jumps for poly(vinyl acetate) (PVAc) in the glass transition region [10]. The above equations are all in linear form and could not describe the nonlinearity character of relaxation dynamics.

To describe the structure dependence of the relaxation time, fictive temperature proposed by Tool [11] is the most widely used physical

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quantity for the structure of the material. Phenomenological Tool–Narayanaswamy–Moynihan (TNM) equation [11–13] and Adam–Gibbs (AG) equation [14,15] based on the configurational entropy model of the glass transition [16,17] are the most widely used models for describing the nonlinearity.

The empirical TNM equation is as below:

$$\tau = A\exp\left[\frac{x\Delta h}{RT}+\frac{(1-x)\Delta h}{RT_{\mathrm{f}}}\right] \tag{4}$$

where A, x $(0 < x \leq 1)$, and Δh are model constants, R is ideal gas constant, T and T_{f} are actual and fictive temperatures, respectively. The parameter x in the TNM model is a direct measure of nonlinearity, with $x = 1$ for a linear relaxation. Despite its wide application in the describing relaxation kinetic of different classes of materials, the imperfection is that the parameters have no clear physical meanings compared with other models, such as VFT or AG model.

The relaxation time in the AG model [14,15] is calculated according to the transition probability of cooperative regions based on the configurational theory and formulated as:

$$\tau = A\exp\left[\frac{C}{TS_{\mathrm{C}}}\right] = A\exp\left[\frac{C}{T\int_{T_2}^{T_{\mathrm{f}}}\frac{\Delta C_p}{T}dT}\right] \tag{5}$$

where C is model constant, S_{c} is the molar configurational entropy of the macroscopic sample, T_2 is Kauzmann temperature, ΔC_p is heat capacity difference between liquid and glass, respectively.

TNM and AG models are extensively used in the description of relaxation kinetics, but inconsequential thermal history dependence of model parameters was reported [18,19]. Perfect model that could describe the temperature and structure dependence of the relaxation time of the glass is still being expecting.

The free volume model of glass transition proposed by Fox and Flory [20], Turnbull and Cohen [21] is widely accepted in the field of polymer science, but the report of investigation on relaxation kinetics using which is infrequent. Here we propose equations of relaxation time based on free volume concept under the line of the AG form and explore their application in description of enthalpy relaxation data of polystyrene. The results are compared with the conventional VFT, TNM, AG and Macedo models. We hope to give some new reference for the unresolved topics of relaxation dynamics and glass transition.

2. The new equations and fitting approach

2.1. FV equation

The relaxation time in the AG model is calculated according to the transition probability of cooperative regions with a minimum size of z^* 'particles' (or monomer units):

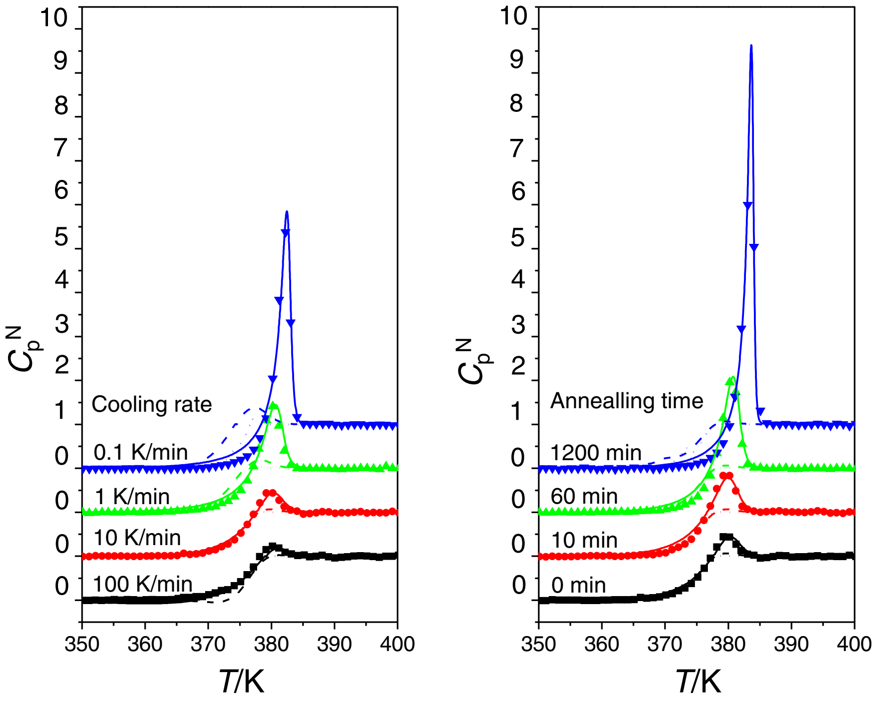
$$\tau = A\exp\left[\frac{z^*\Delta\mu}{kT}\right] \tag{6}$$

where z^* is the smallest number of particles capable of rearranging, $\Delta\mu$ is the elementary excitation energy per particle, and k is the Boltzmann constant, respectively. z^* increases with decreasing temperature and is calculated from the configurational entropy as:

$$z* = \frac{N_{\mathrm{A}}s_{\mathrm{c}}^*}{S_{\mathrm{c}}(T)} \tag{7}$$

where N_{A} is the Avogadro's number, $s_{\mathrm{c}}{}^*$ is the smallest configurational entropy needed for particle rearrangement and S_{c} is the molar configurational entropy of the macroscopic sample.

As pointed out by Hodge [22], a free volume expression can also be formulated using Adam–Gibbs concepts, by defining z^* in terms of the



(a) (b)

Fig. 1. The normalized heat capacity of PS recorded after cooling from 423.15 to 273.15 K at different cooling rates (a) and annealed at 363.15 K for different times (b). The cooling rates and annealing times are reported in the figures. Symbols: experimental data; lines: predicted thermograms using the VFT (dash), VFTf (dot) and FV (solid) models.